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# Method and Apparatus for Direct Determination of Helium-3 in Natural Gas and Helium

By Thomas A. Davidson and David E. Emerson

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BUREAU OF MINES



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**UNITED STATES DEPARTMENT OF THE INTERIOR  
Manuel Lujan, Jr., Secretary**

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## CONTENTS

	<i>Page</i>
Abstract .....	1
Introduction .....	2
Acknowledgments .....	2
Instrumentation .....	2
Gas handling system .....	2
Mass spectrometer .....	4
Calibration for mass identification .....	5
Peak resolution .....	5
Linearity .....	6
Samples .....	7
Analytical procedures .....	10
Analysis of samples for helium-4 .....	10
Analysis of samples for helium-3 .....	10
Instrument preparation .....	10
Calibration standard .....	10
Helium-3 analytical method .....	10
Discussion of results .....	10
Conclusions .....	11
References .....	11
Appendix,—Mass spectrometer inlet conductance .....	12

## ILLUSTRATIONS

1. Apparatus for determining $^3\text{He}$ .....	3
2. Pressure downstream of cryogenic trap .....	4
3. Stable, low-noise electrometer circuit .....	5
4. Resolution of $^3\text{He}$ and the $\text{HD}^+$ peaks .....	6
5. Linearity of the mass spectrometer sensitivity .....	7
6. Bureau of Mines helium conservation pipeline system .....	8
7. Locations of gas wells .....	9
A-1. Mass spectrometer inlet conductance .....	13

## TABLES

1. Total helium and $^3\text{He}$ determinations of pipeline samples .....	8
2. Total helium and $^3\text{He}$ determinations of Bush Dome and Tuck-Trigg Dome .....	8
A-1. Data for determination of conductance .....	12

## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

aA	atto ampere	$\mu$ Pa	micropascal
amu	atomic mass unit	mL/s	milliliter per second
°C	degree Celsius	mm	millimeter
cm	centimeter	min	minute
ft	foot	Pa	pascal
g	gram	Pa-L/s	pascal-liter per second
G $\Omega$	giga ohm	pF	picofarad
k $\Omega$	kilohm	ppb	part per billion
kPa	kilopascal	ppm	part per million
L	liter	ppt	part per trillion
$\mu$ A	microampere	s	second
$\mu$ F	microfarad	V	volt

# METHOD AND APPARATUS FOR DIRECT DETERMINATION OF HELIUM-3 IN NATURAL GAS AND HELIUM

By Thomas A. Davidson<sup>1</sup> and David E. Emerson<sup>2</sup>

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## ABSTRACT

The Bureau of Mines Helium Field Operations has developed a method for determining the helium-3 (<sup>3</sup>He) content of natural gas and mixtures containing 0.5% to 100% helium. The helium is preconcentrated by passing samples through anhydrous, a liquid-nitrogen-cooled charcoal trap, and a titanium absorption trap. The mass spectrometer used to analyze the samples is tuned to <sup>3</sup>He at  $m/e = 3.016$ . Hydrogen deuteride ( $HD^+$ ) interference is minimized by the titanium absorption trap and high instrument resolution. Sample measurements are compared with identically made measurements of a gravimetrically prepared primary standard. The method has a limit of detection of 0.15 ppb with a relative deviation of 13% below the 1-ppb level. The relative deviation is less than 7% for gases containing over 100 ppb <sup>3</sup>He.

The helium isotope ratios of natural gases from the Bureau's Tuck-Trigg Dome Red Cave, the Bush Dome Red Cave, and the Bush Dome Brown Dolomite Formations are distinguishable from one another and from the isotope ratio of crude helium produced from the Panhandle-Hugoton Gasfield.

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## INTRODUCTION

Isotopic variations in neon, argon, and nitrogen have been used by the Bureau of Mines to characterize helium-bearing gases (1-2).<sup>3</sup> The <sup>3</sup>He isotope found in all known natural sources of helium is only a small fraction compared to the helium-4 (<sup>4</sup>He) isotope; however, the processes known to produce the two isotopes are different (3).

The isotopic composition of helium varies the most of all natural samples of elements. The differences in the <sup>3</sup>He/<sup>4</sup>He isotope ratio have been used to characterize sources of various gases, to compare various minerals (4), to trace oceanic currents (5), to characterize areas of tectonic activity (6), and to describe the history of meteorites (7). Variations in a large natural gasfield have been used to describe flow within the field (8-9). These differences are large enough to distinguish helium-bearing gases from different sources even when they occur close together.

The differences in the <sup>3</sup>He content of helium are usually determined as <sup>3</sup>He/<sup>4</sup>He ratios and are obtained by comparison to the <sup>3</sup>He/<sup>4</sup>He ratio in near-surface atmospheric air ( $R_A$ ) (10). Clarke (11) reported a value for  $R_A$  of  $1.384 \times 10^{-6} \pm 0.4\%$ .

Neir measured the <sup>3</sup>He/<sup>4</sup>He ratio with a dual-collector mass spectrometer (12). This instrument detects the two isotopes simultaneously with different detectors. Because of the great difference in abundance of the isotopes, the detectors are of different types, introducing another

possible source of error. The above value of  $R_A$  was obtained with this type of instrument.

An early effort by Coon (13) to measure <sup>3</sup>He directly by neutron activation required large samples and was susceptible to interference by nitrogen. The direct determination of <sup>3</sup>He by mass spectrometry is made difficult by the overwhelming abundance of <sup>4</sup>He, the difficulty of obtaining an accurate standard, and interference by the HD<sup>+</sup> ion, the ion with the mass-charge ratio nearest to that of the singly ionized <sup>3</sup>He produced in mass spectrometers.

The Bureau has developed a method for the direct determination of <sup>3</sup>He in gases in the part-per-trillion range (14). This method uses a single-focusing mass spectrometer with a single detector to make direct measurements of the <sup>3</sup>He content of the sample and gravimetrically prepared standards of similar composition (15). Sample preparation and instrument resolution eliminate the interference of the HD<sup>+</sup> ion. This report describes a modified version of the Bureau method for determining <sup>3</sup>He in the range of 0.5 to 200 ppb (16). Another Bureau method determines <sup>4</sup>He as total helium (17).

Using the method described in this report, the helium isotope ratios have been determined for samples collected from gas wells in the Bureau's Cliffside Field and from privately owned crude helium plants. The results suggest that precise isotope ratio determinations can provide information not previously available about the sources of natural gases.

## ACKNOWLEDGMENTS

The authors would like to express their appreciation to C. A. Seitz and the late E. T. Suttle of the Bureau of

Mines, Helium Field Operations, for their assistance in developing the instrumentation for <sup>3</sup>He determinations.

## INSTRUMENTATION

The instrumentation consists of a gas-handling system incorporating several purification traps, a modified mass spectrometer, and a data system interfaced to a personal computer.

### GAS HANDLING SYSTEM

The gas-handling system (fig. 1) is constructed of welded stainless steel with metal-gasketed fittings and indium seals to avoid contamination due to the high diffusivity of helium through glass and polymers.

Accurate determination of the amount of gas used for each sample requires removal of moisture. A moisture removal trap (B) is installed between the sample cylinder manifold and the sample expansion volume. The trap consists of a 0.95-cm-inside-diameter by 24-cm-long tube of stainless steel containing approximately 15 g of anhydrous magnesium perchlorate (anhydrone). Tests indicated that this trap will dry 216 L of saturated gas to a moisture content of approximately 7 ppm before the anhydrone is exhausted. It has been established that this trap does not affect <sup>3</sup>He measurements (14). During analyses the sample and calibration standards are passed through the trap before entering the sample expansion volume where the pressure is measured.

<sup>3</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix.



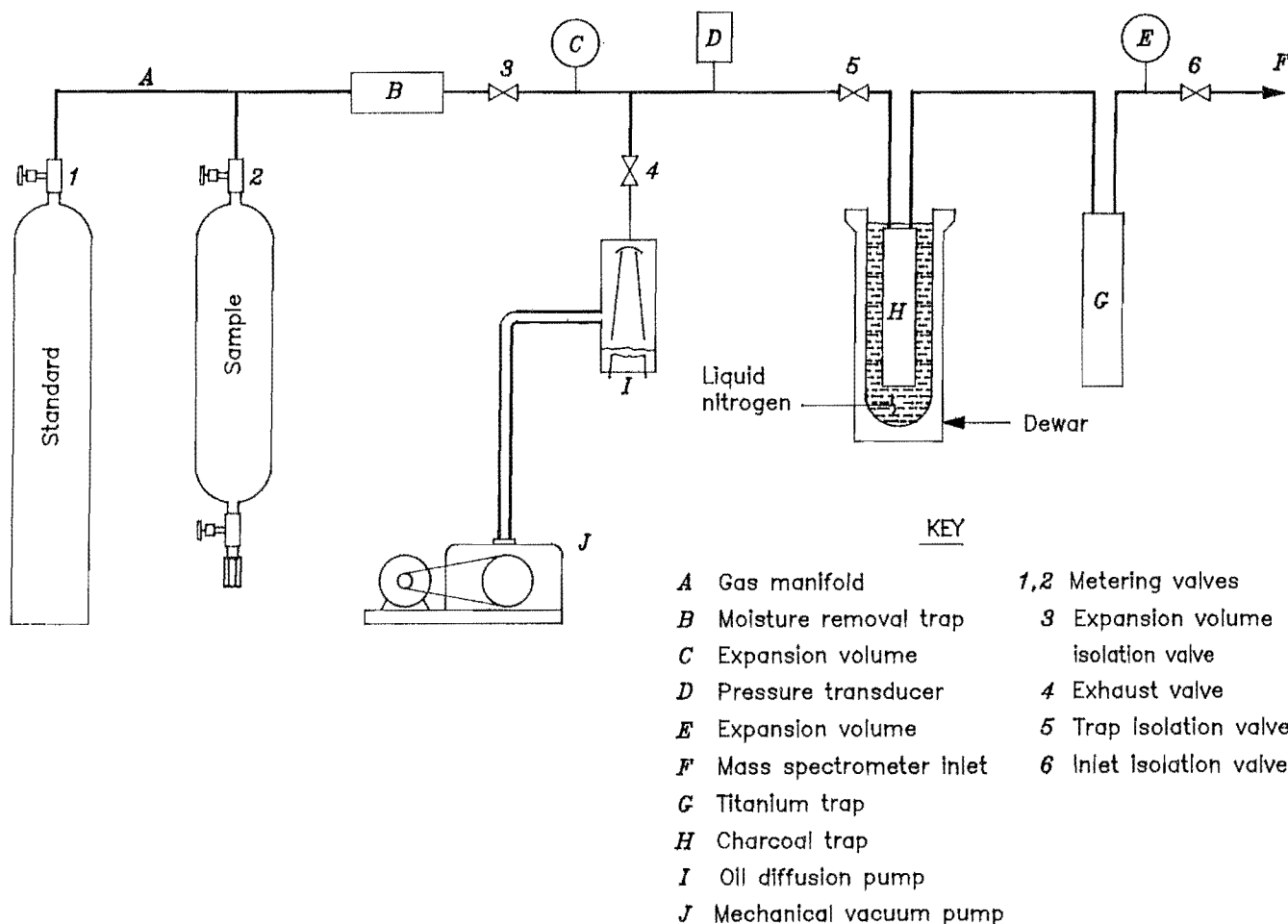


Figure 1.—Apparatus for determining of  $^3\text{He}$  in natural gas.

The sample expansion volume, isolated by valves 3, 4, and 5, has been determined to be 3.176 L. Sample pressures in this volume are measured with a pressure transducer (D). Output is displayed on an electronic manometer accurate to  $\pm 0.01\%$ .

A charcoal trap (H) is used to remove all gases except helium and hydrogen (14). This trap is precooled under vacuum while submerged in liquid nitrogen. After the sample is metered into the sample expansion volume, valve 5 is opened to admit the gas into the charcoal and titanium traps.

A trap (G) consisting of a 0.95-cm-internal-diameter by 23-cm-long stainless steel tube containing 6 g of titanium wire is installed downstream of the cryogenic charcoal trap for removal of hydrogen (18). A 1-L expansion volume (E) permits the collection of the relatively larger quantities of helium compared to previous work without increasing the ultimate pressure of the sample. Valve 6 isolates the gas-handling system from the mass spectrometer.

Timing protocols were established to measure the background while the sample was being preconcentrated, to measure the sample only after optimum pressure had been established, and to complete measurement before cryopumping could reduce the sample pressure. To establish the optimum timing for operating the traps, another pressure sensor was temporarily installed in the place of expansion volume (E). Outdoor air was selected to test the traps. Outdoor air contains 5.2204 ppm  $^4\text{He}$  (19) and 7.27 ppt  $^3\text{He}$  (14), which does not generate excessive pressure in the reduced volume downstream of the titanium trap. Air samples were metered into the inlet system and then admitted to the charcoal trap. The pressure in the sample expansion volume was then monitored until a limiting value was reached. Repeating this procedure at various pressures established that the system could remove all gases except helium from a 3.33-kPa air sample in the sample expansion volume. After regeneration of the traps, a 3.33-kPa sample of air was metered into the inlet system.

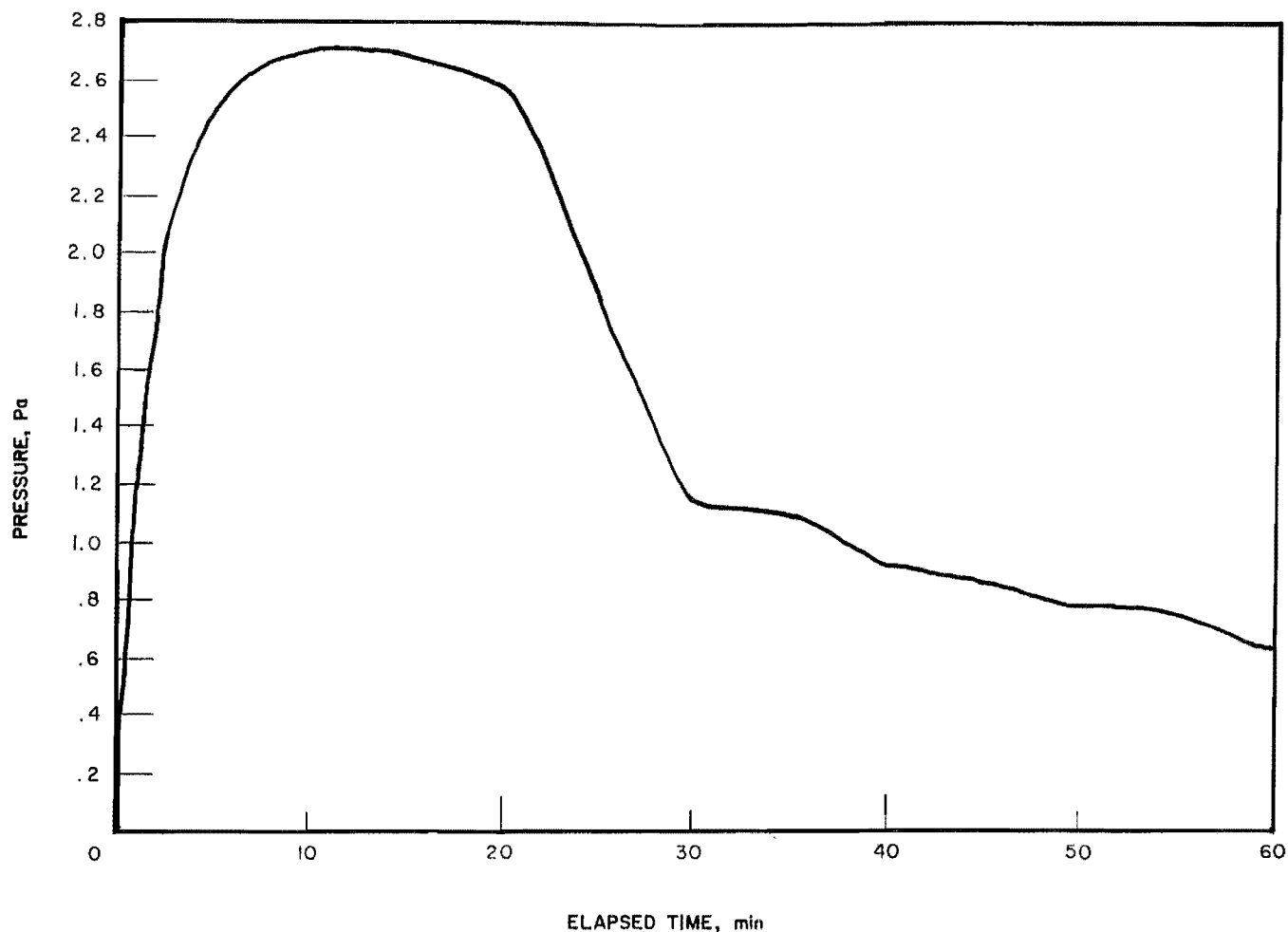


Figure 2.—Pressure downstream of cryogenic trap during sample preconcentration.

The air sample was then admitted, and the pressure downstream of the traps was monitored as a function of time (fig. 2). The pressure required 12 min to reach peak value as helium accumulated and remained above 95% of peak value for 8 min. The drop after 20 min is taken as an indication of cryopumping. Timing of the system starts at the opening of valve 5. Background data collection starts 10 min after preconcentration has begun and is complete at 13 min. Exactly 30 s are allotted for processing the background data. Sample data collection starts at 13:30 min and is complete at 19:30 min.

The orifice that limits the flow of sample into the ion source of the mass spectrometer is a gold foil with a hole of approximately 0.03-mm diameter. To ensure linear response of the instrument, it was necessary to determine the maximum pressure for molecular flow through the

orifice. Under conditions of molecular flow, the conductance of the orifice is constant. The value of this constant is the low pressure limit of the conductance. The rate of change of pressure ( $dP/dt$ ) in the inlet system as a function of pressure is sufficient to establish this limit (20). The procedure described in the appendix was used to determine the conductance of the orifice. The conductance is within 1% of its limiting value at pressures below 266.6 Pa. Helium pressure after the preconcentration step was kept below this value for all  $^3\text{He}$  determinations.

### MASS SPECTROMETER

A single-focusing magnetic sector mass spectrometer has been modified to increase both stability and sensitivity. A copper-beryllium plate electron multiplier with 20 stages

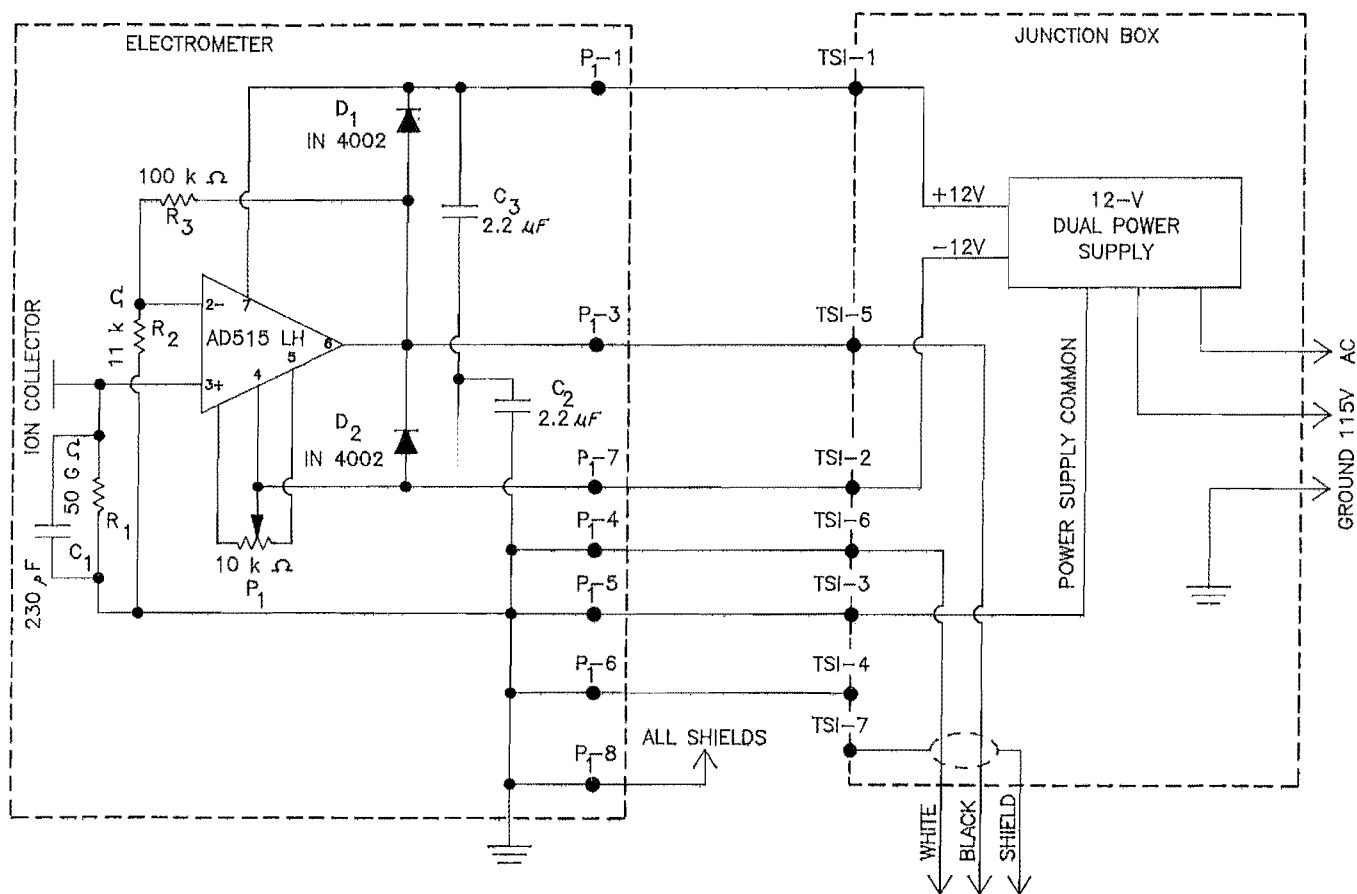


Figure 3.—Stable, low-noise electrometer circuit for mass spectrometer.

amplifies the ion current by 100,000. A high-voltage power supply with 0.005% stability controls the electron multiplier gain. A specially designed electrometer utilizing a stable, low-noise integrated circuit (fig. 3) is mounted on the electron multiplier in a machined iron container. A programmable power supply that is stable to 1 part in 16,000 provides accelerating voltage to the ion source. The constant current supply for the magnet current is stable to 1 part in 18,000. A data system interfaced to a personal computer controls the ion accelerating voltage and digitizes and processes the electrometer output. A dual-pen recorder provides a simultaneous analog record. The vacuum system maintains the pressure in the analyzer assembly below  $4 \mu\text{Pa}$ . The heat emitted by the filament is sufficient to maintain the ion source assembly at  $145 \pm 1^\circ \text{C}$ .

### Calibration for Mass Identification

The mass spectrometer is calibrated daily for mass identification by scanning the background of the  $\text{HD}^+$  ion (mass to charge ratio  $m/e = 3.0218$ ) at a rate of 0.05 mass unit per minute. A data bandwidth of 0.0005 mass unit is achieved with the data system by assigning a "mass" of 6,044 units to the  $\text{HD}^+$  ion peak in the mass calibration option. The  $^3\text{He}$  peak ( $m/e = 3.0160$ ) then occurs at a "mass" of 6,032 units.

### Peak Resolution

The mass spectrometer resolution was set by adjusting focus and repeller voltages to minimize the ratio of peak

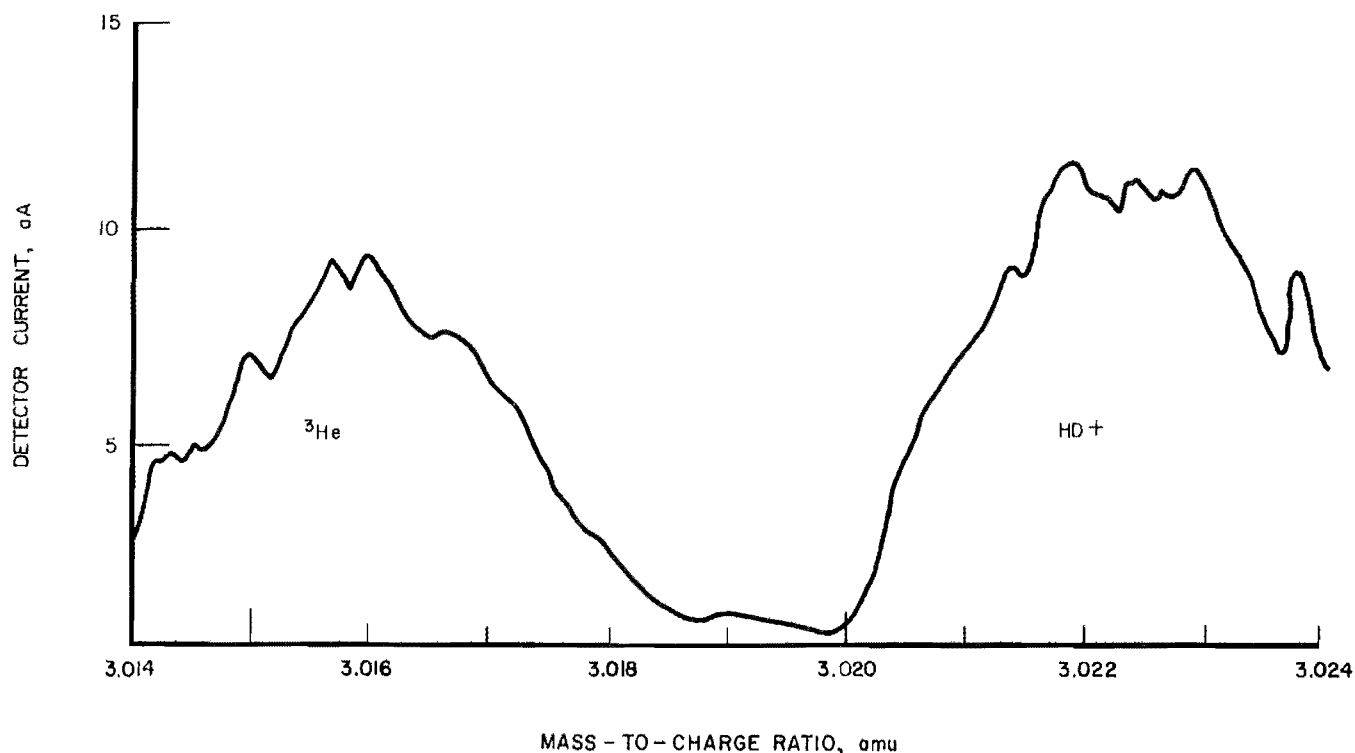


Figure 4.—Resolution of  $^3\text{He}$  and the  $\text{HD}^+$  peaks in scan from  $m/e = 3.014$  to  $m/e = 3.024$ .

width to peak height for the  $\text{HD}^+$  ion background. The detector slit width was then reduced until the  $\text{HD}^+$  ion background peak width was minimized without loss of peak height. Optimum slit width was determined to be 0.635 mm. Finally, the Wein filter plate voltages were adjusted to maximize peak height. The electrometer output at 6,044, 6,032, and 6,020 showed that the contribution of the  $\text{HD}^+$  ion background at 6,032 units was less than 0.01% of the value at the  $\text{HD}^+$  ion peak. Thus the maximum contribution for  $\text{HD}^+$  ion is approximately 0.01% relative to the  $^3\text{He}$  peak. Figure 4 shows the results of a scan from 6,028 units to 6,048 units with 26.66 Pa of helium in the sample expansion volume containing 108.7 ppb  $^3\text{He}$ . These adjustments achieve baseline resolution of the  $^3\text{He}$  and  $\text{HD}^+$  ion peaks. Tests on standards containing less than 10 ppt  $^3\text{He}$  show that the  $\text{HD}^+$  ion background after preconcentration does not measurably affect the  $^3\text{He}$  measurements.

### Linearity

The linearity of the method was confirmed by analyzing a series of nine gravimetric standard mixtures of  $^3\text{He}$  in  $^4\text{He}$ , covering a range from 1.36 ppb to 1,541 ppb  $^3\text{He}$ . Three standard mixtures with less than 200 ppb  $^3\text{He}$  were each analyzed at two different inlet pressures to check for pressure dependence of the sensitivity. Four standard mixtures with more than 200 ppb  $^3\text{He}$  were analyzed twice each at the same pressure to determine the repeatability of the measurements. The repeatability of these measurements was 5%. The sensitivity of the mass spectrometer to  $^3\text{He}$  was constant within the repeatability of the measurements at inlet pressures from 13.33 to 533.3 Pa. The relative sensitivity is shown in figure 5 to be within 5% of the average value over a range of three orders of magnitude.

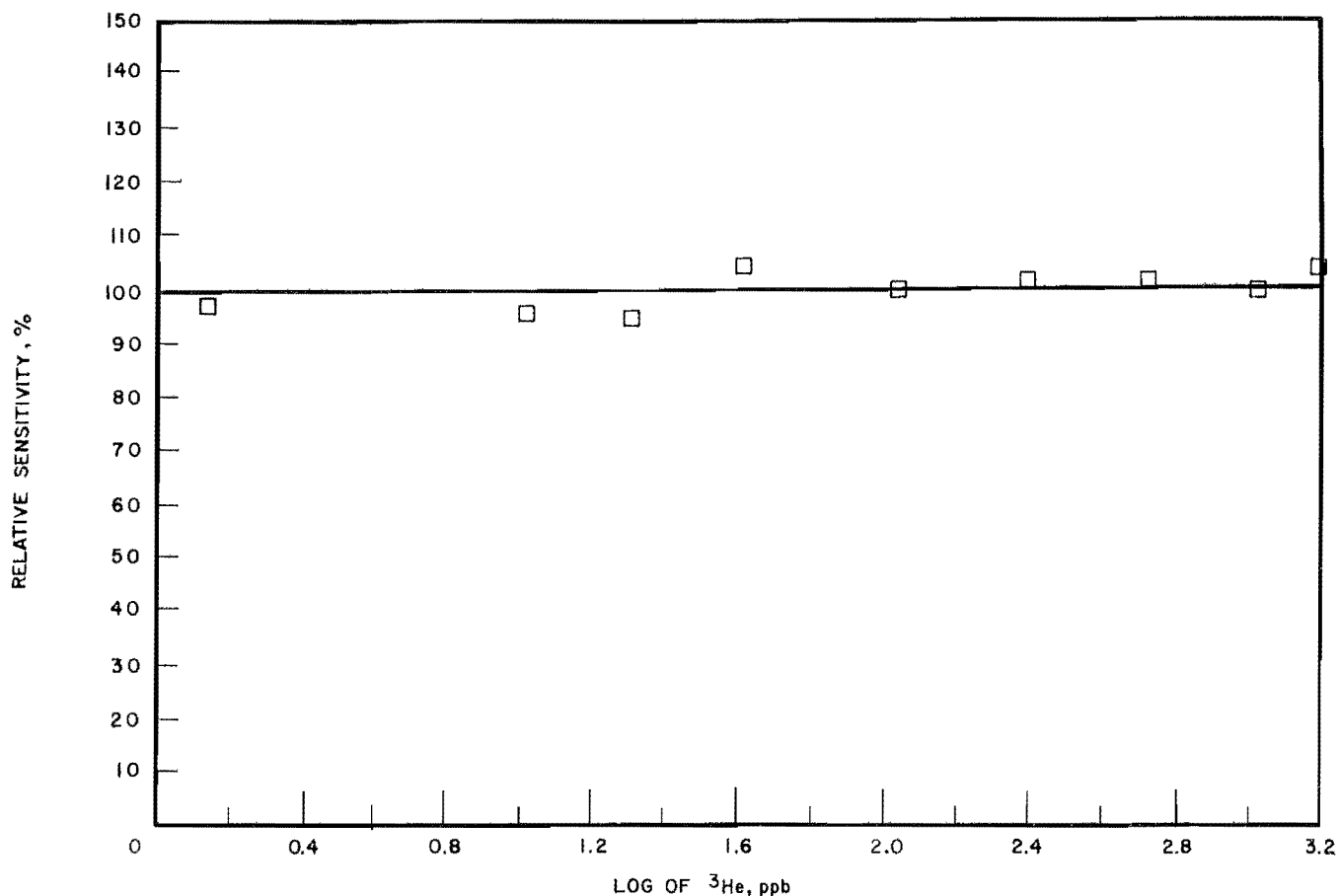


Figure 5.—Linearity of the mass spectrometer sensitivity to  $^3\text{He}$  over three orders of magnitude.

## SAMPLES

Measurements were made of the total helium and  $^3\text{He}$  content of samples of crude helium collected at several points along the Bureau's helium conservation pipeline where privately owned plants that supply crude helium are connected (fig. 6). Measurements were also made of samples from gas wells located in the Cliffside Field, Potter County, TX (fig. 7).

Tables 1 and 2 list the results of the total helium and  $^3\text{He}$  analyses and the calculated  $^3\text{He}/^4\text{He}$  ratios.

All pipeline samples were collected in April 1988. The pipeline samples show no signs of air contamination. They are identified by a plant number and the date taken.

Samples from wells in the Cliffside Field (fig. 7) were collected from May through July 1988. The wells Bivins A-9, A-11, and B-2; Bush A-8, A-9, A-10, A-11, and B-1; and Fuqua A-1 and A-2 are completed in the Brown

Dolomite Formation around the periphery of Bush Dome. All show total helium content that is approximately the same as the original helium content of the field. This indicates that these wells contain native gas not invaded by crude helium injected into the field by the Bureau as part of the helium conservation program.

Bivins A-8R is completed in the Red Cave Formation in the Cliffside Field about 450 ft above the apex of Bush Dome. The total helium content is comparable to that of the Bush Dome Brown Dolomite Formation native gas.

The four wells Bush B-2R, Bush B-3R, USBM-1R, and USBM-2R are located in the Tuck-Trigg Dome approximately 6 miles northeast of the center of the Bush Dome. These wells are completed in the Red Cave Formation and are used solely for producing of natural gas for fuel.

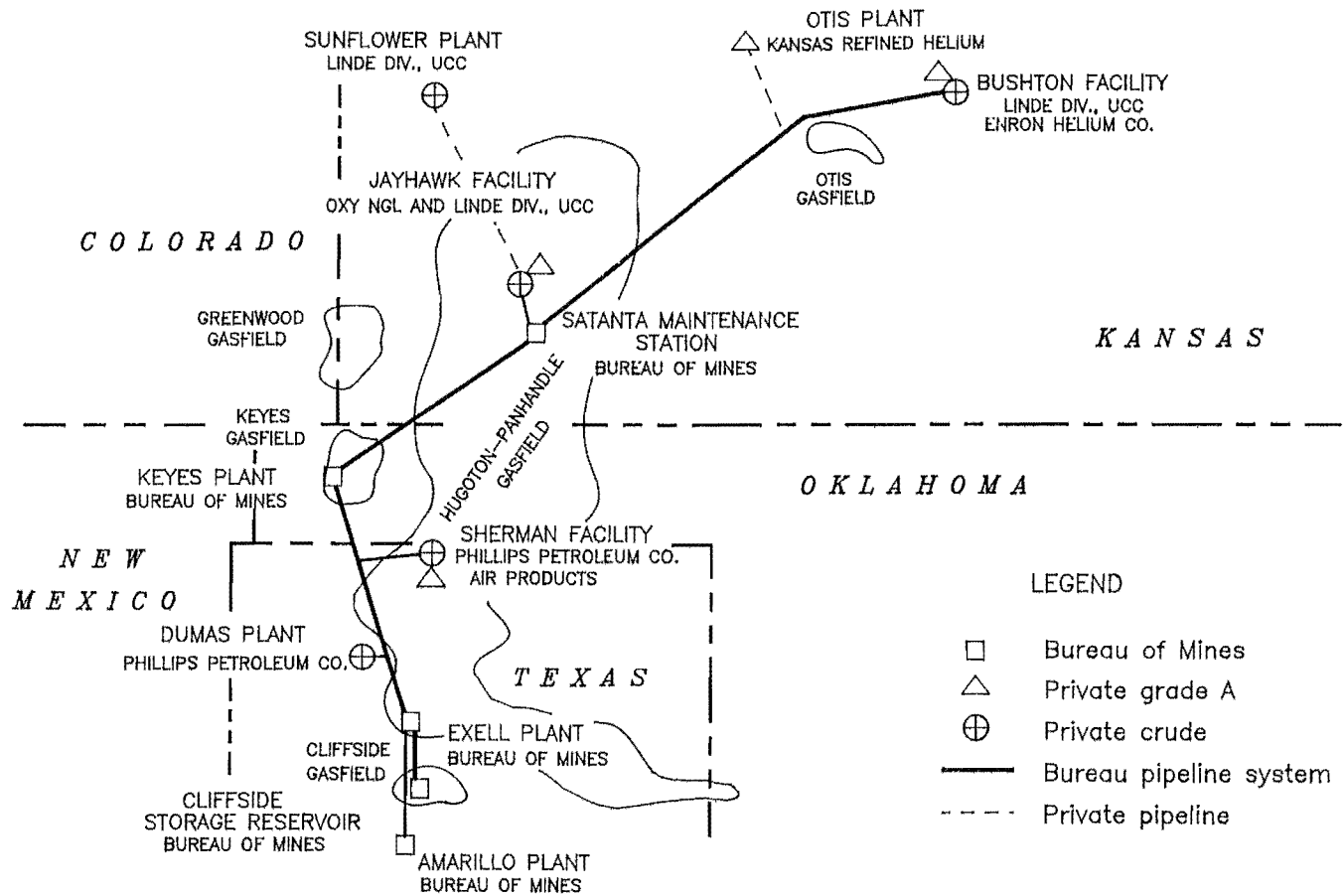


Figure 6.—Bureau of Mines helium conservation pipeline system.

Table 1.—Total helium and  $^3\text{He}$  determinations of pipeline samples from commercial helium plants, with calculated  $^3\text{He}/^4\text{He}$  ratios

Sample	Total He, %	$^3\text{He}$ , ppb	$^3\text{He}/^4\text{He}$ , $\times 10^6$
Plant 1-4/16 .....	74.74	152	0.203
Plant 1-4/20 .....	77.07	161	.209
Plant 1-4/24 .....	82.51	200	.242
Plant 1-4/27 .....	75.17	146	.194
Plant 1-4/31 .....	76.92	161	.209
Plant 2-4/11 .....	77.30	172	.222
Plant 2-4/17 .....	76.95	166	.216
Plant 2-4/24 .....	76.17	134	.176
Plant 2-4/30 .....	75.72	152	.201
Plant 3-4/07 .....	75.23	149	.198
Plant 3-4/14 .....	78.09	147	.188
Plant 3-4/20 .....	79.08	152	.192
Plant 3-4/28 .....	74.55	148	.199
Plant 3-4/30 .....	82.72	179	.216
Plant 4-4/10 .....	52.58	110	.209
Plant 5-4/16 .....	60.66	124	.204
Plant 5-4/21 .....	52.28	109	.208
Plant 5-4/27 .....	75.16	152	.202

Table 2.—Total helium and  $^3\text{He}$  determinations of Bush Dome and Tuck-Trigg Dome, with calculated  $^3\text{He}/^4\text{He}$  ratios

Sample	Total He, %	$^3\text{He}$ , ppb	$^3\text{He}/^4\text{He}$ , $\times 10^6$
Bivins A-9 .....	1.990	2.87	0.144
Bivins A-11 .....	1.928	2.62	.136
Bivins B-2 .....	1.945	2.70	.139
Bush A-8 .....	1.877	2.84	.151
Bush A-9 .....	1.715	2.73	.159
Bush A-10 .....	1.903	2.68	.141
Bush A-11 .....	1.847	2.51	.136
Bush B-1 .....	1.828	2.61	.143
Fuqua A-1 .....	1.844	2.38	.129
Fuqua A-2 .....	1.876	2.54	.135
Bivins A-8R .....	1.878	2.38	.127
Bush B-2R .....	.629	.59	.094
Bush B-3R .....	.626	.48	.077
USBM-1R .....	.626	.44	.070
USBM-2R .....	.649	.54	.083

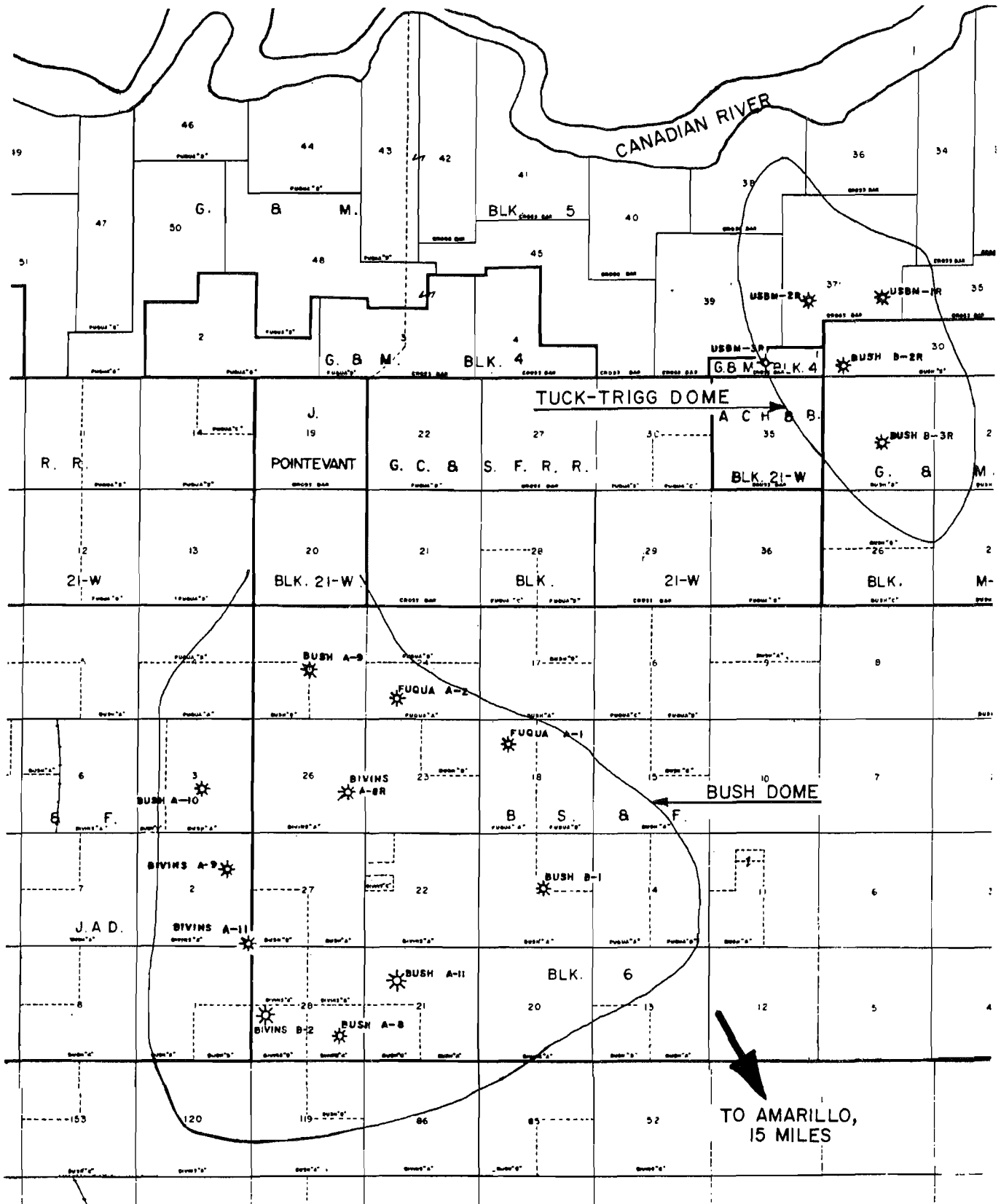


Figure 7.—Locations of gas wells in the Cliffslope Field, Potter County, TX.

## ANALYTICAL PROCEDURES

### ANALYSIS OF SAMPLES FOR HELIUM-4

Samples with less than 10% helium were chromatographically analyzed for helium content. Samples with 10% or more helium were analyzed for total helium content with the special helium analyzer (17). Because the ratio of total helium to  $^3\text{He}$  content exceeded  $10^6$ , the total helium content was taken as the  $^4\text{He}$  content.

### ANALYSIS OF SAMPLES FOR HELIUM-3

The total helium content is used to determine the pressure for the  $^3\text{He}$  analysis, called the metering pressure. The metering pressure is selected so that the residue pressure of the helium, after passing the sample through the purification traps, will be in the range 133.3 to 266.6 Pa. Helium pressures in this range were determined to provide maximum instrument sensitivity.

#### Instrument Preparation

The procedures for startup of the instrument follow: The pressure in the analyzer is verified to be below  $4\ \mu\text{Pa}$ . The ionizing current is raised to  $40\ \mu\text{A}$ , and the heater on the titanium is turned off. At least 45 min is required for thermal stabilization of the analyzer assembly and cooling of the titanium trap. The cryogenic charcoal trap is submerged in liquid nitrogen. This prepares the instrument for operation.

#### Calibration Standard

The calibration standard was prepared from  $^3\text{He}$ ,  $^4\text{He}$ , and methane by a gravimetric method of successive dilutions (15, 21). The standard was selected to represent a  $^3\text{He}$  concentration close to the expected median of the samples. A standard of  $3.280 \pm 0.023\ \text{ppb}\ ^3\text{He}$  and  $7.9845 \pm 0.0047\% \ ^4\text{He}$  in methane was selected.

#### Helium-3 Analytical Method

The  $3.28\text{-ppb-}^3\text{He}$  standard is analyzed three times at the start of each set of measurements to determine the sensitivity. The sensitivity is defined as the ratio of the signal measured to the product of the pressure and the  $^3\text{He}$  concentration in the standard. This is followed by at least three analyses of the unknown.

To assure consistent treatment, a standardized procedure has been established for sample preparation and handling for both the sample and the standard gas. With valves 4 and 5 closed, the gas to be analyzed is passed through the moisture removal trap (B) to the sample expansion volume at a pressure exceeding the metering pressure. The sample is isolated in the expansion volume (C) with valve 3. The pressure is reduced to the metering pressure as measured by the transducer (D) by opening valve 4, producing the gas aliquot to be admitted to the purification traps. The following sequence of actions is taken on a rigid time schedule: At 0:00 min valve 5 is opened. Simultaneously the dewar surrounding the charcoal trap is topped off with liquid nitrogen. The gas aliquot then contacts the charcoal at  $-197^\circ\text{C}$ , and then the titanium at  $25^\circ\text{C}$ , before entering the collection volume (E). At 2:30 min, 5:00 min, 7:30 min, and 9:45 min, the dewar is topped off with liquid nitrogen. At 10:00 min the collection of the background data is initiated. The background data consist of the electrometer output voltage from 10:00 min to 13:00 min. The background data are then processed, and the average value is calculated and stored. At 13:30 min, valve 6 is opened and the collection of  $^3\text{He}$  data for the aliquot is initiated. At 19:30 min the  $^3\text{He}$  data for the aliquot are processed and stored. The processed  $^3\text{He}$  data consist of two successive 3-min averages of the electrometer output voltage. The charcoal trap is then reactivated by heating to  $100^\circ\text{C}$ , while the entire gas-handling system is evacuated to less than  $13\ \mu\text{Pa}$ .

Control of the data processing is automatically passed from the data acquisition software to the computer operating system. A FORTRAN program reads the stored data, subtracts the background from the  $^3\text{He}$  data, and sums the  $^3\text{He}$  data to provide a measure of the  $^3\text{He}$ . The digitized data, the results of these calculations, and identifying data for the analysis are printed.

If the relative deviation of a set of three analyses is greater than 10%, one or more additional analyses are performed until the relative deviation drops below this value. A single datum is allowed to be dropped only if it is more than two standard deviations from the mean of the remainder of the set, with at least three values in the remaining set. If the relative deviation does not drop below 10% for the set as a result of this procedure, the entire set is discarded and the sample reanalyzed. A set of three analyses requires 100 min to perform.

## DISCUSSION OF RESULTS

The analyses of 18 helium conservation pipeline samples are presented in table 1. The total helium content ranges from 52.28% to 82.72% for these samples. The  $^3\text{He}/^4\text{He}$  ratio is remarkably constant. The average ratio of  $^3\text{He}$  to  $^4\text{He}$  is  $0.205 \times 10^{-6}$ , with a standard deviation of  $0.014 \times 10^{-6}$ .

These data are consistent with independent determinations (2) of the isotope ratio in the gases processed by these plants, suggesting a single source for the helium. The relative deviation of the ratios is 6.8%.



The analyses of samples collected from gas wells in the Bureau's Cliffside Field are presented in table 2. The 10 wells completed into the periphery of the Bush Dome (Bivins A-9, A-11, and B-2; Bush A-8, A-9, A-10, A-11, and B-1; and Fuqua A-1 and A-2) have essentially the same total helium contents and isotope ratios. The average  $^3\text{He}/^4\text{He}$  ratio for these samples is  $0.141 \times 10^{-6}$ , with a standard deviation of  $0.009 \times 10^{-6}$ . This ratio is significantly lower than that of the pipeline samples. The relative deviation of the ratios is 6.4%.

Although the total helium content of Bush A-8R is comparable to that of Bush Dome native gas, the  $^3\text{He}$  content is significantly lower. The isotope ratio is  $0.127 \times 10^{-6}$ , suggesting that the gas has a different origin.

The gas samples from the Tuck-Trigg Dome show the lowest  $^3\text{He}/^4\text{He}$  ratios found in this study. The average of the values obtained for the isotope ratio of Tuck-Trigg gas is  $0.081 \times 10^{-6}$ , with a standard deviation of  $0.010 \times 10^{-6}$ . The Tuck-Trigg gas also has the lowest total helium content. This identifies the Tuck-Trigg Dome Red Cave gas as having a source of helium distinct from that of the Bush Dome Red Cave gas 6 miles to the southwest.

The average  $^3\text{He}$  content of the Tuck-Trigg Dome wells is 0.513 ppb, with a standard deviation of 0.066 ppb. The relative deviation for the  $^3\text{He}$  is 13%, and the limit of detection is 0.15 ppb.

## CONCLUSIONS

The Bureau has developed a method for determining the  $^3\text{He}$  content of natural gas and mixtures containing 0.5% to 100% helium. This method uses a mass spectrometer to compare the  $^3\text{He}$  contents of a sample gas and a gravimetrically prepared standard. The method has a limit of detection of 0.15 ppb with a relative error of 13% below the 1-ppb level. The relative error is less than 7% for gases containing over 100 ppb  $^3\text{He}$ .

The  $^3\text{He}/^4\text{He}$  ratios of natural gases from the Bureau's Tuck-Trigg Dome Red Cave, the Bush Dome Red Cave, and the Bush Dome Brown Dolomite Formations are distinguishable from one another and from that of crude helium produced by commercial plants located in the Panhandle-Hugoton Gasfield.

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## APPENDIX.-MASS SPECTROMETER INLET CONDUCTANCE

The following procedure was used to determine the conductance (K) of the orifice of the mass spectrometer inlet before installing the 1-L expansion volume. The volume (V) of the inlet system, including the sample expansion volume and the charcoal and titanium traps, was determined to be 3.278 L. The inlet system was filled with helium to 1.34 kPa. Valve 6 was opened, and the pressure was allowed to equalize. A pressure reading ( $P_1$ ) was taken simultaneously with starting a stopwatch. The pressure was allowed to fall for at least 40 s to over 1,000 s, depending on the rate of fall, to obtain a pressure change in V of at least two significant figures. A second pressure reading ( $P_2$ ) was taken when the watch was stopped. Both initial and final pressures were recorded, as well as the elapsed time ( $\Delta t$ ). Valve 4 was then opened to remove some of the sample in the expansion volume, and the process was repeated. The value of  $dP/dt$  was determined by dividing the difference between the pressure readings  $P_2$  and  $P_1$  by the time interval  $\Delta t$ . The effective

pressure (P) is the average of  $P_1$  and  $P_2$ . The flow rate (Q) was then determined as  $-V \cdot dP/dt$  and the conductance (K) as  $Q/P$ .

The data indicated there was a small leak (q) into the inlet system of 0.00507 Pa-L/s. By using an adjusted flow rate (Q') equal to  $Q + q$ , the adjusted conductance (K') became essentially constant at the value  $0.7028 \pm 0.0019$  mL/s for pressures below 266.6 Pa. The leak q would be expected to contribute 1.333 Pa of air to the 3.2-L inlet system over a span of 810 s. This leak was located and sealed.

The data are summarized in table A-1. Figure A-1 shows the dependence of the conductance on pressure using a logarithmic pressure scale. The conductance of the inlet orifice is within 1% of its limiting value at pressures below 266.6 Pa. Helium pressure after the preconcentration step was kept below this value for all  $^3\text{He}$  determinations.

TABLE A-1.-Data for determination of conductance of mass spectrometer inlet

$P_1$ , Pa	$P_2$ , Pa	$\Delta t$ , s	Q, Pa-L/s	Q', Pa-L/s	K, mL/s	log(P)
1,339.	1,326.	43.33	1.0084	1.0135	0.7603	3.1248
1,206.	1,193.	48.73	.8966	.9017	.7516	3.0790
1,073.	1,059.	55.02	.7941	.7992	.7494	3.0279
939.7	926.4	63.53	.6877	.6928	.7425	2.9699
806.4	793.1	75.06	.5821	.5872	.7342	2.9029
673.1	659.8	91.44	.4778	.4829	.7245	2.8238
539.8	526.5	115.31	.3789	.3840	.7202	2.7268
406.5	393.2	155.31	.2813	.2864	.7162	2.6019
273.2	259.9	238.25	.1834	.1884	.7069	2.4258
206.6	193.2	322.88	.1353	.1404	.7021	2.3009
133.9	132.6	49.32	.0885	.0936	.7026	2.1248
120.6	119.1	60.71	.0791	.0842	.7025	2.0788
107.3	105.9	62.37	.0700	.0751	.7045	2.0279
93.84	92.51	72.57	.0602	.0652	.7006	1.9693
80.64	79.31	85.03	.0513	.0564	.7059	1.9029
67.31	65.98	104.85	.0416	.0467	.7013	1.8238
53.98	52.65	135.33	.0322	.0373	.7006	1.7268
40.65	39.32	190.39	.0229	.0280	.7006	1.6019
27.32	25.99	318.64	.0137	.0187	.7045	1.4258
20.66	19.32	486.03	.0089	.0140	.7031	1.3009
13.99	12.66	1,019.16	.0042	.0093	.7019	1.1248

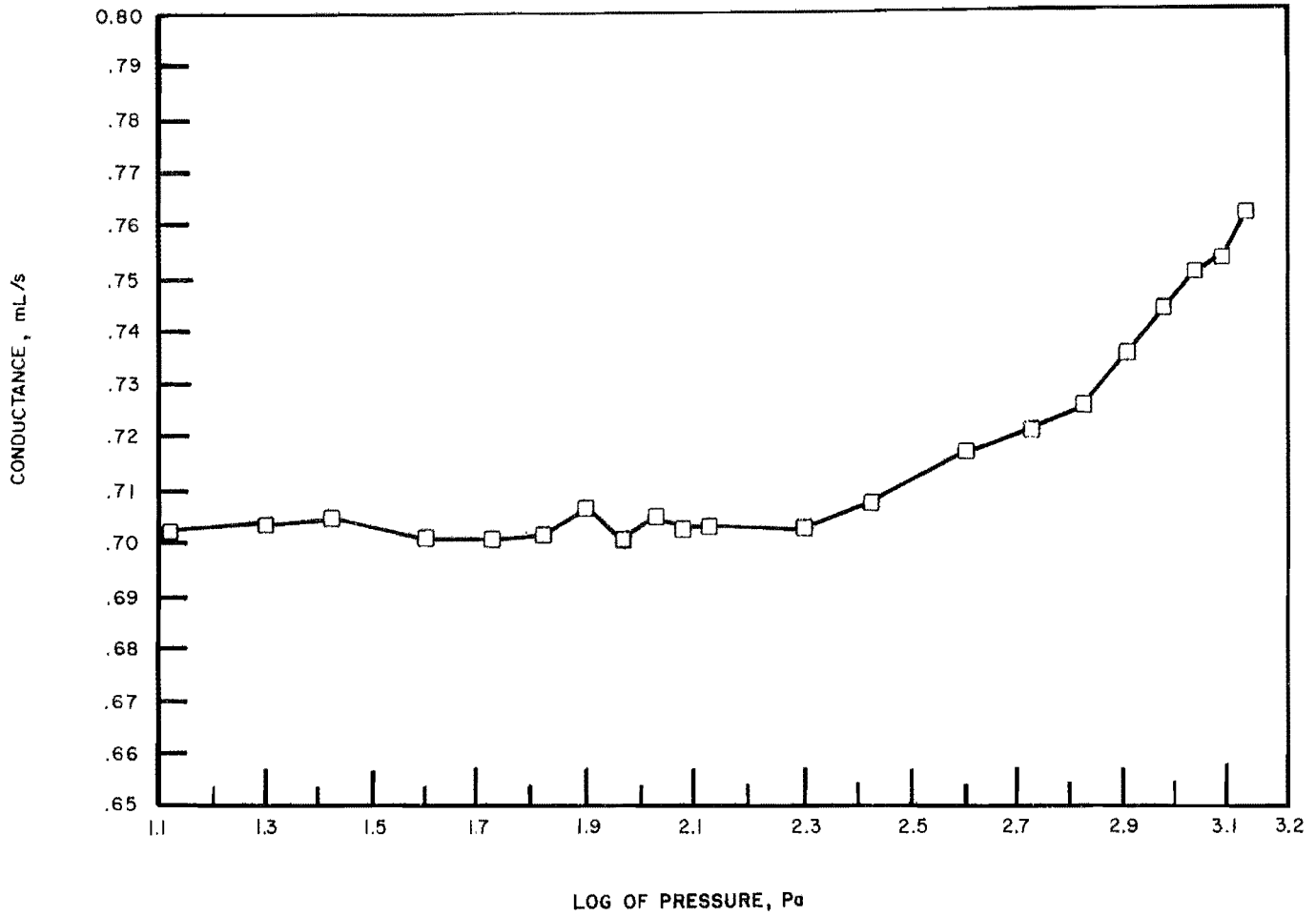


Figure A-1.--Mass spectrometer inlet conductance as a function of pressure at inlet.